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(54) **METHOD FOR MANUFACTURING ZIRCONIUM OXIDE FILM FOR USE IN SEMICONDUCTOR DEVICE**

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(58) **Field of Search** 438/765, 778, 438/785, 758

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PUBLICATIONS

Kukli et al., "Low-temperature deposition of zirconium oxide-based nanocrystalline films by alternate supply of $Zr[OC(CH_3)_3]_4$ and H_2O ", *Chemical Vapor Deposition*, vol. 6, Nov. 2000, pp 297-302.*

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(57) **ABSTRACT**

A method for manufacturing a zirconium oxide film for use in a semiconductor device by using an atomic layer deposition (ALD) which begins with setting a wafer in a reaction chamber. Thereafter, a zirconium source material of $Zr(OC(CH_3)_3)_4$ (zirconium tetra-tert-butoxide) is supplied into the reaction chamber and then, an unreacted $Zr(OC(CH_3)_3)_4$ is removed by a N_2 purge or a vacuum purge. Subsequently, an oxygen source material is supplied into the reaction chamber, wherein the oxygen source material is selected from the group consisting of vaporized water (H_2O), O_2 gas, N_2O gas and O_3 gas. Finally, an unreacted oxygen source material is purged out from the reaction chamber.

24 Claims, 1 Drawing Sheet

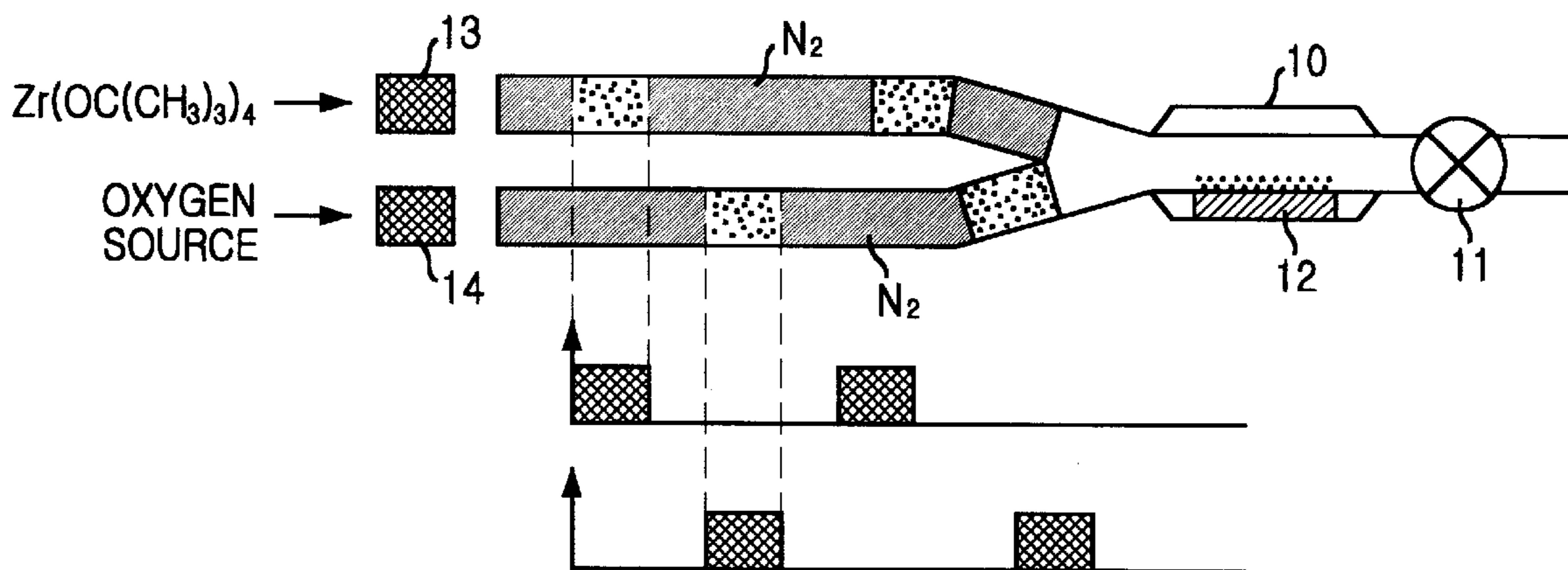
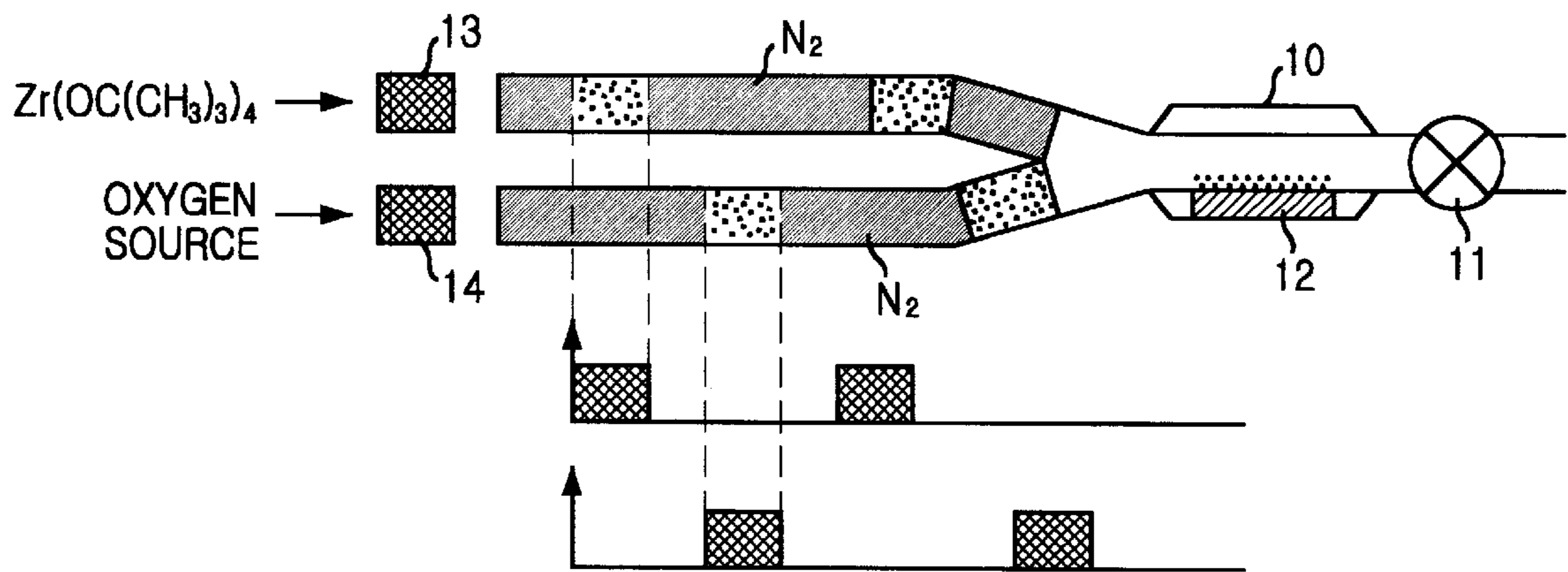


FIG. 1



METHOD FOR MANUFACTURING ZIRCONIUM OXIDE FILM FOR USE IN SEMICONDUCTOR DEVICE

FIELD OF THE INVENTION

The present invention relates to a semiconductor device and, more particularly, to a method for manufacturing a zirconium oxide film for use in a semiconductor device by using $Zr(OC(CH_3)_3)_4$ (zirconium tetra-tert-butoxide) as a zirconium oxygen source material in place of conventional $ZrCl_4$.

DESCRIPTION OF THE PRIOR ART

Generally, in a semiconductor memory device, various dielectric materials are used for a gate oxide film and a capacitor thin film so that dielectric properties mainly affect derivability of the semiconductor memory device.

With high integration and high speed of the semiconductor memory device, research has been undertaken for application of a titanium oxide (TiO_2) or an aluminum oxide (Al_2O_3) as the dielectric material in place of a conventional silicon oxide (SiO_2).

A zirconium oxide (ZrO_2) film has been applied to the gate oxide film of the semiconductor memory devices with high integration. The zirconium oxide is formed by using an atomic film deposition (ALD) technique. Conventionally, $ZrCl_4$ and vaporized water (H_2O) are used as a zirconium source material and an oxygen source material, respectively.

In more detail, a conventional manufacturing method for forming the zirconium oxide film includes the steps of setting a wafer in a reaction chamber; heating the wafer up to a predetermined temperature; supplying the zirconium source material of $ZrCl_4$ into the reaction chamber; purging out unreacted $ZrCl_4$; supplying the oxygen source material of vaporized H_2O into the chamber; and purging out unreacted vaporized H_2O . This is one cycle for depositing the zirconium oxide film. By repeating this cycle, the intended thickness of the zirconium oxide film is obtained.

However, since the conventional method utilizes $ZrCl_4$ as the zirconium source material, the zirconium oxide film of the prior art has a disadvantage in that there are chlorines (Cl) remaining in the zirconium oxide film. As a result, an electrical property of the device is degraded and an agglomeration of the zirconium oxide film is apt to occur. In addition, the $ZrCl_4$ is characteristically in a solid state at room temperature and it is melted at a temperature of $437^\circ C$. and a pressure of 25 atm. Therefore, it is difficult to supply the $ZrCl_4$ into the reaction chamber in a gaseous state.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a method for manufacturing a zirconium oxide film by using $Zr(OC(CH_3)_3)_4$ (zirconium tetra-tert-butoxide) as a zirconium source material instead of conventional $ZrCl_4$, thereby inhibiting the remainder of chlorine in the zirconium oxide film.

In accordance with one aspect of the present invention, there is provided a method for manufacturing a zirconium oxide film for use in a semiconductor device by using an atomic layer deposition (ALD), the method comprising steps of a) setting a wafer in a reaction chamber; b) supplying a zirconium source material of $Zr(OC(CH_3)_3)_4$ into the reaction chamber; c) purging out unreacted $Zr(OC(CH_3)_3)_4$; d) supplying an oxygen source material into the reaction chamber; and e) purging out unreacted oxygen source material.

In accordance with another aspect of the present invention, there is provided a method for manufacturing a zirconium oxide film for use in a semiconductor device by using an atomic layer deposition (ALD), the method comprising steps of a) setting a wafer in a reaction chamber; b) supplying a zirconium source material of $Zr(OC(CH_3)_3)_4$ into the reaction chamber; c) purging out unreacted $Zr(OC(CH_3)_3)_4$; d) supplying nitrogen species gas into the reaction chamber; and e) purging out unreacted nitrogen species gas.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become apparent from the following description of the preferred embodiments given in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view of an apparatus for forming a zirconium oxide film in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, there is provided a schematic view of an apparatus for forming a zirconium oxide film in accordance with a preferred embodiment of the present invention. The manufacturing steps begin with setting a wafer **12** in a reaction chamber **10** provided with a discharging pump **11**. Thereafter, $Zr(OC(CH_3)_3)_4$ (zirconium tetra-tert-butoxide) is supplied as a zirconium source material into the reaction chamber **10** for a period of approximately 0.1 seconds to approximately 3 seconds while the wafer heats up to a temperature ranging from approximately $250^\circ C$. to approximately $450^\circ C$. and the $Zr(OC(CH_3)_3)_4$ is absorbed on a surface of the wafer **12**.

In a next step, in order to purge out any unreacted $Zr(OC(CH_3)_3)_4$ and a by-product, nitrogen gas (N_2) is supplied into the reaction chamber **10** for a period of approximately 0.1 seconds to approximately 5 seconds. Here, a high vacuum purging process may be carried out instead of the N_2 purging process.

In a subsequent step, an oxygen source material is supplied into the reaction chamber **10** for a period of approximately 0.1 seconds to approximately 5 seconds, whereby the oxygen source material is absorbed on the surface of the wafer **12**. It is preferable that the oxygen source material include vaporized water (H_2O), O_2 gas, N_2O gas, O_3 gas or the like.

Thereafter, in order to purge out any unreacted oxygen source material and a by-product, nitrogen gas (N_2) is supplied into the reaction chamber **10** for a period of approximately 0.1 seconds to approximately 5 seconds. Here, the high vacuum purging process may also be carried out instead of the N_2 purging process.

This represents one cycle for depositing the zirconium oxide film. By repeating this cycle numerous times, an intended thickness of the zirconium oxide film may be obtained. It is preferable that a pressure in the reaction chamber **10** should be kept within a range of approximately 100 mtorr to approximately 3 Torr. Here, reference numerals **13**, **14** denote a vessel for storing the $Zr(OC(CH_3)_3)_4$ and a vessel for storing the oxygen source material, respectively.

Meanwhile, NH_3 gas as an active gas can be supplied into the reaction chamber **10** simultaneously, with a flux rate of 20 standard cubic centimeters per minute (sccm) to 1,000 sccm, when the $Zr(OC(CH_3)_3)_4$ is supplied. At this time, separate supply-pipes should be used. If NH_3 gas and the

Zr(OC(CH₃)₃)₄ are supplied into the reaction chamber **10** through the same supply-pipe, the Zr(OC(CH₃)₃)₄ reacts with the NH₃ gas, thereby producing particles in the supply-pipe.

While supplying the oxygen source material, NH₃ gas as the active gas also can be supplied into the reaction chamber **10** simultaneously through the same supply-pipe. If NH₃ gas is not supplied into the reaction chamber **10** through the same supply-pipe as used for the oxygen source material, lots of particles may be produced.

NH₃ gas may also be supplied simultaneously when the Zr(OC(CH₃)₃)₄ and the oxygen source material are supplied into the reaction chamber **10** under the same conditions aforementioned. It is noted that the active gas can be substituted by mixed gas of H₂ and N₂ instead of NH₃ gas.

Finally, after the deposition reaction, carbon (C), hydrogen (H) particles or other impurities may exist in the zirconium oxide film, thereby degrading a resulting electrical property. Thus, the following process is carried out to avoid deterioration of the electrical property using a method such as O₂ plasma, N₂O plasma, UV/O₃ or the like.

Since the Zr(OC(CH₃)₃)₄ has oxygen atoms therein, the zirconium oxide film may be formed without using the oxygen source material such as H₂O, O₂, N₂O or O₃. At this time, NH₃ or H₂+N₂ gas is supplied into the reaction chamber **10** through the supply-pipe of the oxygen source material. That is, the steps include supplying the Zr(OC(CH₃)₃)₄; N₂ purging; supplying NH₃ gas; N₂ purging or vacuum purging. In addition, NH₃ gas and the Zr(OC(CH₃)₃)₄ can also be supplied into the reaction chamber simultaneously through their respective supply-pipes.

In comparison with the prior art, the inventive method uses the Zr(OC(CH₃)₃)₄ as the zirconium source material. As a result, it is possible to inhibit chlorine residues after deposition, thereby preventing degradation of the electrical property and an agglomeration of the zirconium oxide film. Furthermore, the Zr(OC(CH₃)₃)₄ has a boiling point of approximately 900° C. so that it is not difficult to supply the Zr(OC(CH₃)₃)₄ into the reaction chamber in a gaseous state. In addition, the active gas used in the inventive method, e.g., NH₃ or a mixed gas of H₂ and N₂, reacts with the Zr(OC(CH₃)₃)₄, thereby forming a hydrocarbon such as CH₄, CH₃ or the like. Thus, this active gas accelerates the decomposition of the zirconium or oxygen source material and reduces the concentration of impurities in the zirconium oxide film.

Although the preferred embodiments of the invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

What is claimed is:

1. A method for manufacturing a zirconium oxide film for use in a semiconductor device by using an atomic layer deposition (ALD), the method comprising steps of:

- a) setting a wafer in a reaction chamber;
- b) supplying a zirconium source material of Zr(OC(CH₃)₃)₄ (zirconium tetra-tert-butoxide) into the reaction chamber;
- c) purging out unreacted Zr(OC(CH₃)₃)₄;
- d) supplying an oxygen source material into the reaction chamber;
- e) purging out unreacted oxygen source material; and
- f) carrying out a process using an oxygen gas plasma selected from the group consisting of UV—O₃, N₂O, O₂ and O₃.

2. The method as recited in claim **1**, wherein the steps b) to e) are repeated several times until the zirconium oxide film is formed to a predetermined thickness.

3. The method as recited in claim **1**, wherein the Zr(OC(CH₃)₃)₄ is supplied simultaneously with NH₃ gas into the reaction chamber through respective supply-pipes.

4. The method as recited in claim **3**, wherein a flux of NH₃ gas ranges from approximately 20 sccm to approximately 1,000 sccm.

5. The method as recited in claim **1**, wherein the Zr(OC(CH₃)₃)₄ and a mixed gas of hydrogen gas (H₂) and nitrogen gas (N₂) are supplied simultaneously into the reaction chamber through respective supply-pipes.

6. The method as recited in claim **5**, wherein a flux of the mixed gas of H₂ and N₂ ranges from approximately 20 sccm to approximately 1,000 sccm.

7. The method as recited in claim **1**, wherein the oxygen source material is supplied simultaneously with NH₃ gas into the reaction chamber through a common supply-pipe.

8. The method as recited in claim **7**, wherein a flux of NH₃ gas ranges from approximately 20 sccm to approximately 1,000 sccm.

9. The method as recited in claim **1**, wherein the oxygen source material and a mixed gas of hydrogen gas (H₂) and nitrogen gas (N₂) are supplied simultaneously into the reaction chamber through a common supply-pipe.

10. The method as recited in claim **9**, wherein a flux of the mixed gas of H₂ and N₂ ranges from approximately 20 sccm to approximately 1,000 sccm.

11. The method as recited in claim **1**, wherein the oxygen source material is selected from the group consisting of vaporized water (H₂O), O₂ gas, N₂O gas and O₃ gas.

12. The method as recited in claim **1**, wherein the step c) is carried out by using a method selected from the group consisting of a nitrogen gas (N₂) purge and a vacuum purge.

13. The method as recited in claim **1**, wherein the step e) is carried out by using a method selected from the group consisting of a nitrogen gas (N₂) purge and a vacuum purge.

14. The method as recited in claim **1**, wherein a temperature of the wafer ranges from approximately 250° C. to approximately 450° C.

15. The method as recited in claim **1**, wherein a pressure in the reaction chamber ranges from approximately 100 mTorr to approximately 3 Torr.

16. The method as recited in claim **1**, wherein the steps b) and d) are each carried out for a period of approximately 0.1 seconds to approximately 5 seconds.

17. The method as recited in claim **1**, wherein the steps c) and e) are each carried out for a period of approximately 0.1 seconds to approximately 5 seconds.

18. A method for manufacturing a zirconium oxide film for use in a semiconductor device by using an atomic layer deposition (ALD), the method comprising steps of:

- a) setting a wafer in a reaction chamber;
- b) supplying a zirconium source material of Zr(OC(CH₃)₃)₄ into the reaction chamber;
- c) purging out unreacted Zr(OC(CH₃)₃)₄;
- d) supplying nitrogen species gas into the reaction chamber; and
- e) purging out unreacted nitrogen species gas.

19. The method as recited in claim **18**, wherein the nitrogen species gas is selected from the group consisting of NH₃ gas and a mixed gas of H₂ and N₂.

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20. The method as recited in claim 18, wherein the steps b) to e) are repeated several times until the zirconium oxide film is formed to a predetermined thickness.

21. The method as recited in claim 18, after the step e), further comprising the step of carrying out an oxygen gas plasma selected from the group consisting of UV—O₃, N₂O, O₂ and O₃.

22. The method as recited in claim 18, wherein the Zr(OC(CH₃)₃)₄ is supplied simultaneously with NH₃ gas into the reaction chamber through respective supply-pipes.

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23. The method as recited in claim 18, wherein the Zr(OC(CH₃)₃)₄ and a mixed gas of H₂ and N₂ are supplied simultaneously into the reaction chamber through respective supply-pipes.

24. The method as recited in claim 18, wherein the step c) is carried out by using a method selected from the group consisting of a nitrogen gas (N₂) purge and a vacuum purge.

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